PCT/EP 99 / 0 8 0 5 5



4

EP99/80055

# Kongeriget Danmark

Patent application No.: PA 1998 01398

Date of filing: 30 Oct 1998

Applicant: Haldor Topsøe A/S
Nymøllevej 55
DK-2800 Lyngby

This is to certify the correctness of the following information:

The attached photocopy is a true copy of the following document:

- The specification, claims, abstract and drawings as filed with the application on the filing date indicated above.

Patent- og Varemærkestyrelsen
Kongeriget Danmark

**Patent- og Varemærkestyrelsen**
Erhvervsministeriet

TAASTRUP 14 Oct 1999

Lizzi Vester
Head of Section

**PRIORITY DOCUMENT**
SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

HALDOR TOPSØE A/S

NYMØLLEVEJ 55 . P. O. BOX 213 . DK-2800 LYNGBY . COPENHAGEN . DENMARK . CABLE ADDRESS: HALTOPS
TELEPHONE: +45 45 27 20 00 . TELECOPIER: +45 45 27 29 99 . TELEX: 37 444 HTAS DK . REG.NO. 52370

30 October 1998
DK2687237003

# Process and Converter for the Preparation of Ammonia

The present invention relates to the preparation of ammonia by catalytic conversion of ammonia synthesis gas.

More particularly, this invention concerns synthesis of ammonia at high conversion rates of ammonia synthesis gas in presence of an ammonia synthesis catalyst arranged in a tubular reaction zone being cooled by a cooling agent on shell side of the tubular reaction zone. Synthesis of ammonia from synthesis gas of hydrogen and nitrogen is an exothermic process and the process requires cooling to obtain high conversion rates.

Even if the concentration of hydrogen and nitrogen in the synthesis gas is close to the stoichiometric composition for ammonia formation, complete reaction to ammonia cannot be obtained by a single passage of the synthesis gas through a catalytic bed. Furthermore, due to the exothermic nature of the ammonia synthesis, increasing temperature during passage through the catalytic bed displaces the equilibrium concentration towards lower ammonia concentration. Several methods for cooling the ammonia synthesis process are known.

The usual methods are by either indirect or direct cooling of the synthesis gas between series of catalytic beds wherein the ammonia synthesis proceeds an ammonia synthesis catalyst.

By direct cooling, cold synthesis gas is introduced into partly reacted synthesis gas between the beds. The disadvantage of this cooling method is dilution of the partly reacted gas with unreacted gas resulting in lower ammonia concentration in the product stream from the process.

In the indirect cooling method, the partly reacted synthesis gas is cooled by cold gas, usually fresh synthesis gas in a heat exchanger arranged between outlet and inlet of two catalytic beds.

It has now been found that conversion rate of ammonia synthesis gas to ammonia is much improved when cooling the synthesis as it proceeds in a catalytic bed of ammonia synthesis catalyst by heat transfer to a cooling agent being in heat contact with the process.

Accordingly, this invention provides a process for the preparation of ammonia comprising steps of:

contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as reaction zone in one or more catalyst tubes;

cooling the reaction zone by heat conducting relationship with a cooling agent; and

withdrawing an ammonia rich effluent stream from the reaction zone.

In its most general embodiment, the above process is carried out in a converter with one or more catalyst tubes arranged in a shell for retaining cooling agent. Synthesis gas is introduced at top of the catalyst tube and passed through the reaction zone with the ammonia synthesis catalyst. Heat being developed during conversion of the hydrogen and nitrogen in the synthesis gas to ammonia is continuously transferred through wall of the catalyst tube to the cooling medium surrounding the tube. By continuous cooling of the process, an adiabatic temperature increase is substantially avoided and the process is then carried out at substantially isothermal conditions resulting in higher conversion rates of the synthesis gas to ammonia than in the known ammonia synthesis processes with indirect or direct cooling of partially reacted synthesis gas, where the cooled gas is contacted with the catalyst at adiabatic conditions. Having removed heat of reaction from the reaction zone, the cooling medium is continuously or periodically withdrawn from the converter and externally cooled

by e.g. heat exchange with water or steam and recycled to the converter by conventional means.

In a specific embodiment of the invention, the cooling agent is retained in a space formed by outer wall of the catalyst tube and inner wall of a cooling tube concentrically surrounding the catalyst tube.

As an advantageous feature of the latter embodiment shell of a reactor with a number of catalyst tubes can be avoided or made from material with considerably lower mechanical strength than in the conventional ammonia converters.

Preferably, the cooling tubes surrounding the catalyst tubes are designed with a lower mechanical strength than the catalyst tube. In case of catalyst tube rupture reacting gas escaping at high pressure into the space between the catalyst and cooling tube, the gas pressure of the cooling tube and the gas ventilate into a space surrounding the cooling tube. Thereby, the synthesis gas depressurizes outside the cooling tubes and contact with the cooling agent is reduced advantageously.

Furthermore, the invention provides a converter for the preparation of ammonia by conversion reaction of ammonia synthesis gas in presence of an ammonia synthesis catalyst and cooling the reaction as it proceeds on the synthesis catalyst, the converter comprises at least one catalyst tube adapted to receive the ammonia synthesis gas and to hold a reaction zone with the ammonia synthesis catalyst, which at least one catalyst tube being arranged in a container with a cooling agent.

Cooling media being useful as cooling agent in the above process will be any solid or liquid having a melting point below the temperature in the reaction zone, including salt or mixture of salts, metals or liquids being inert at the actual process conditions including eutectic mixtures

of salts like mixtures of $KNO_3$, $NaNO_3$ and $NaNO_2$ (supplied by Degussa) and eutectic mixtures of NaOH and KOH. Further eutectic salt mixtures and cooling liquids are well known in the chemical industry. The usual temperature condition in the process will be between 300°C and 600°C and the temperature of the cooling agent has to be maintained at a predetermined level within this temperature range by external cooling of the agent as mentioned herein before.

Removal of ammonia from the ammonia rich product gas being withdrawn from the catalyst tubes is by further an embodiment of the invention obtained through adsorption on an adsorbent having high affinity to ammonia at high pressure, such as regeneration of the spent adsorbent is carried out through depressurization of the adsorbent and recovery of ammonia rich gas similar to separation of e.g. oxygen or nitrogen in the known pressure swing adsorption processes. Furthermore, ammonia may be separated from unconverted synthesis gas by cooling and condensation of ammonia in the ammonia rich effluent stream from the process. Unreacted synthesis gas being separated from ammonia in the product gas may then be recycled to the catalyst tube or passed to a subsequent catalyst tube for further conversion.

**CLAIMS**

1. Process for the preparation of ammonia comprising steps of

contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as reaction zone in one or more catalyst tubes;

cooling the reaction zone by heat conducting relationship with a cooling agent; and

withdrawing an ammonia rich effluent stream from the reaction zone.

2. The process of claim 1, wherein the ammonia synthesis gas is contacted with the ammonia synthesis gas arranged in two or more reaction zones with intermediate withdrawal of an ammonia rich effluent stream between the reaction zones.

3. The process of claim 1, wherein the ammonia rich effluent stream is separated in a stream of unconverted ammonia synthesis gas and an ammonia product stream, the unconverted ammonia synthesis gas is recycled to the reaction zone.

4. The process of claim 2 and 3, wherein the separation is obtained by cooling of the effluent stream and condensation of ammonia.

5. The process of claim 2 and 3, wherein the separation is obtained by adsorption of ammonia contained in the effluent stream.

6. The process of claim 1, wherein the cooling agent is circulated within cooling tubes, each surrounding concentrically one catalyst tube.

7. The process according to anyone of the preceding claims, wherein the cooling agent is selected from salts, metals and liquids having a melting point below the temperature in the reaction zone.

8. The converter for the preparation of ammonia comprising at least one catalyst tube adapted to receive ammonia synthesis gas and to hold a reaction zone of ammonia synthesis catalyst; and

a cooling agent at shell side of the catalyst tubes.

9. The process of claim 8, further comprising at least one cooling tube concentrically surrounding the catalyst tube(s) and adapted to hold the cooling agent.

10. The converter of claim 9, wherein wall of the cooling tube(s) is designed with a lower mechanical strength than wall of the catalyst tube(s).

**ABSTRACT**

Process for the preparation of ammonia comprising steps of

contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as reaction zone in one or more catalyst tubes;

cooling the reaction zone by heat conducting relationship with a cooling agent; and

withdrawing an ammonia rich effluent stream from the reaction zone.

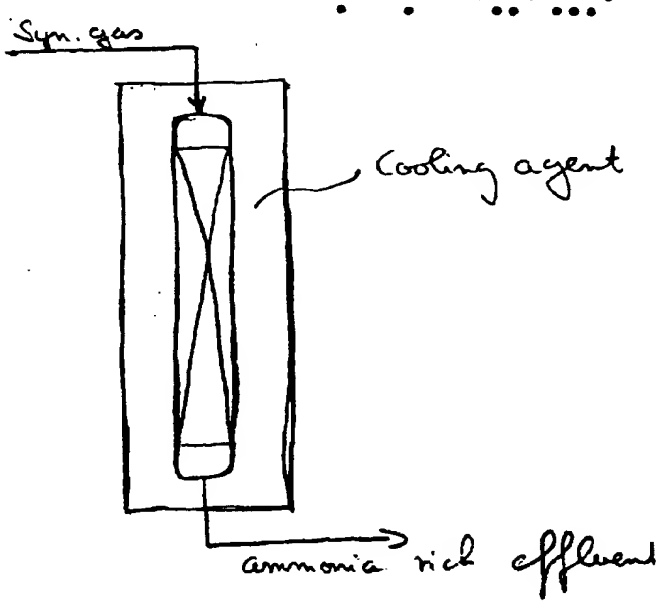


Fig. 1

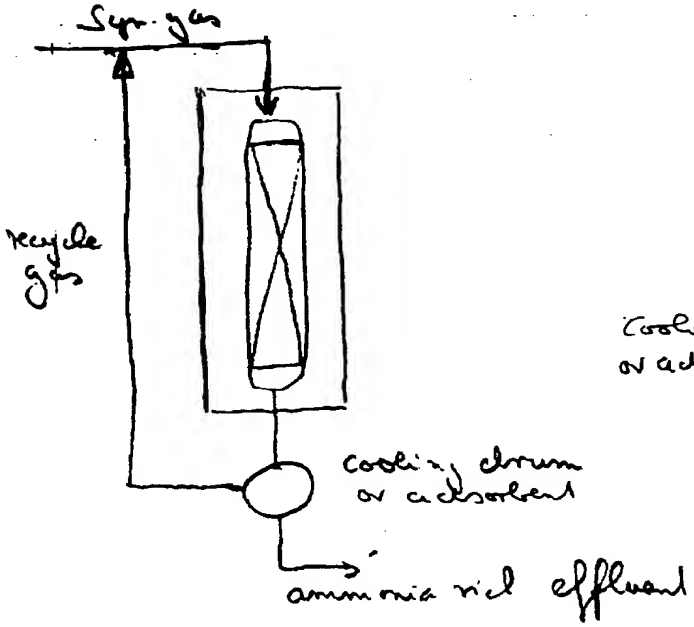


Fig 2

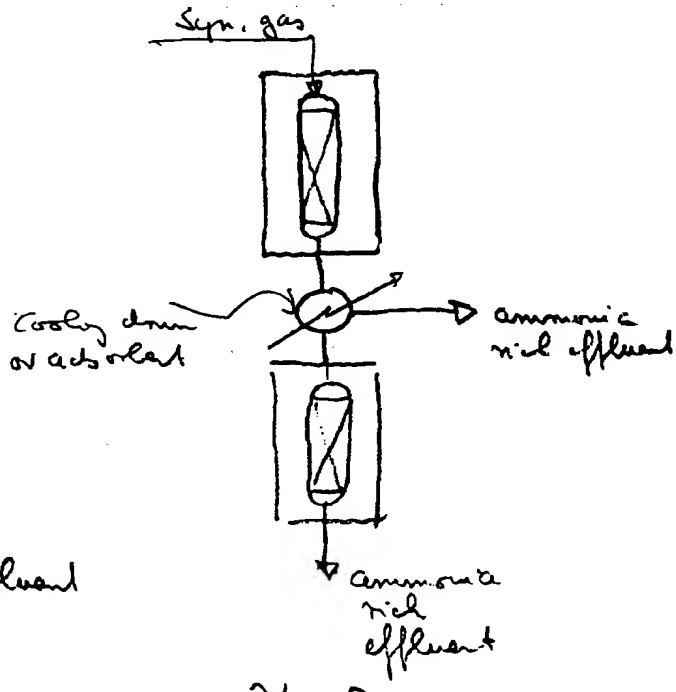


Fig. 3